Neighboring Group Participation in Solvolysis. VII. Trifluoroacetolysis of ω-Phenylalkyl 6-Methyl-2-naphthalenesulfonates*

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The title compounds, $Ph(CH_2)_nOMns$ (n=2—6), were solvolyzed in buffered trifluoroacetic acid in order to elucidate the effect of a phenyl group at a remote position on the reactivity and the course of the reaction. The reactivities varied remarkably with the length of the alkyl chain(n); $2 \gg 3 \ll 4 > 5 > 6$. The rate enhancement was attributed to anchimeric assistance by a remote phenyl group, and the rate depression to the electron-withdrawing inductive effect of a phenyl group. Studies on reaction products revealed that in trifluoroacetolysis of 4-phenylbutyl menasylate (n=4) the only pathway to take place is the one with δ-phenyl participation, and that even for 5-phenylpentyl menasylate (n=5) 12% of the reaction proceeds *via* ε-phenyl participation.

Participation of remote aryl groups in solvolysis has been investigated by Winstein and collaborators with ω-arylalkyl *p*-bromobenzenesulfonates in acetic acid and formic acid.[1] Rate enhancements and formation of cyclic products, however, are not remarkable except when the aryl groups are activated with suitable substituents. Formolysis of 4-phenylbutyl *p*-bromobenzenesulfonate, *e.g.*, proceeded with a comparable rate as that of butyl *p*-bromobenzenesulfonate, and gave only a 17% yield of 1,2,3,4-tetrahydronaphthalene (tetralin). On the other hand, solvents with low-nucleophilicity and high-ionizing power such as trifluoroacetic acid are known to enhance the solvolysis with anchimeric assistance.[2] Recently, Mason reported that a considerable rate enhancement by δ-phenyl participation was detected in trifluoroacetolysis of a series of 1-methyl-ω-phenylalkyl tosylates.[3] He observed a 93% yield of 1-methyltetralin in trifluoroacetolysis of 1-methyl-4-phenylbutyl tosylate. In the case of the secondary tosylates, however, a quantitative discussion is difficult because it can not be denied that the methyltetralin may be produced from the first-formed ion or ion-pair. The present investigation on trifluoroacetolysis of ω-phenylalkyl 6-methyl-2-naphthalenesulfonates was undertaken in order to elucidate quantitatively the effect of a remote phenyl group on the reactivity and the course of the reaction. In this case of the primary esters in the low-nucleophilic solvent, anchimeric assistance must be pronounced and a rate-product correlation must be valid.

Results

By use of a newly-developed leaving group, 6-methyl-2-naphthalenesulfonate (menasylate; Mns), trifluoroacetolysis can be followed easily and accurately by the spectrophotometric method.[4] At the standard substrate concentration (0.05 M) in the presence of 0.125 M of sodium trifluoroacetate, the reaction rates of butyl (**1**) and ω-phenylalkyl menasylates (**2**—**6**) were determined by following decrease in absorption at 326 nm.

$CH_3(CH_2)_3OMns$	$C_6H_5(CH_2)_nOMns$
1	**2** (n=2), **3** (3), **4** (4), **5** (5), and **6** (6)

* A preliminary report of this work was presented at the 32nd National Meeting of the Chemical Society of Japan, Tokyo, April 1975.

The observed rate constants together with the corresponding activation parameters are given in Table 1. Each reported rate constant is the average value of duplicate or triplicate runs. The individual runs have correlation coefficients greater than 0.9995 over two half-lives for all compounds except 3-phenylpropyl menasylate (**3**). In the case of **3**, discoloration of the solution was observed as the reaction proceeded. The rate constants were thus calculated from absorbances observed at the earlier stage of the reaction (up to 50—65%) and those at infinity estimated therefrom.

Reaction products were analyzed by gas chromatography after more than seven half-lives under the same conditions as those for the kinetic runs. Reaction solutions containing dodecane or hexadecane as internal standards were injected directly into a gas chromatograph. The yields of the products corrected with their respective sensitivities are summarized in Table 2. All the products were separated by preparative gas chromatography and identified by comparison with authentic samples or by spectroscopic methods. Control experiments showed that primary trifluoroacetates (**7**, **10**, **12**, and **15**) and hydrocarbons (**9**, **11**, and **14**) were stable under the reaction conditions but a secondary trifluoroacetate (**8**) was unstable under the present reaction conditions.

Discussion

It is evident from Table 1 that the chain length has a decisive influence on the trifluoroacetolysis rates of ω-phenylalkyl menasylates. The phenomenon is more clearly demonstrated in Fig. 1, in which logarithms of the relative rate constants (k_{rel}) of ω-phenylalkyl menasylates to the reference compound, butyl menasylate (**1**), are plotted against the number of the alkyl chain. Similar plots for acetolysis and formolysis of ω-phenylalkyl brosylates are also shown in Fig. 1 for comparison.[1]

Large rate enhancements for **2** and **4**, and a distinct rate depression for **3** both in trifluoroacetolysis are apparent in Fig. 1. With respect to the solvent effect, the order of rate increase observed for **2** is exactly the same order of rate decrease for **3**, *i.e.*, $CF_3CO_2H > HCO_2H > CH_3CO_2H$. Thus a solvent of low-nucleophilicity and high-ionizing power is effective for both the rate enhancement and the rate depression. The rate enhancement must be the result of anchimeric

Table 1. Trifluoroacetolysis rates of ω-phenylalkyl menasylates

Substrate	t/°C	$k_t \times 10^5$/s^{-1}	k_{rel}[a]	ΔH^*/kcal mol^{-1} [b]	ΔS^*/e. u.[c]
$CH_3(CH_2)_3OMns$ (**1**)	100	3.82±0.03	1.00	23.1	−17.2
	110	8.85±0.03			
$C_6H_5(CH_2)_2OMns$ (**2**)	40	2.84±0.01		20.1	−15.1
	50	8.08±0.01			
	60	21.1 ±0.1			
	100	620[d]	162		
$C_6H_5(CH_2)_3OMns$ (**3**)	100	0.99[e]	0.26	24	−18
	110	2.3[e]			
$C_6H_5(CH_2)_4OMns$ (**4**)	60	2.90±0.01		21.2	−15.7
	70	7.46±0.02			
	80	18.9 ±0.1			
	100	100[d]	26.2		
$C_6H_5(CH_2)_5OMns$ (**5**)	100	4.52±0.01	1.18	23.0	−17.3
	110	10.2 ±0.1			
	120	23.2 ±0.2			
$C_6H_5(CH_2)_6OMns$ (**6**)	100	3.99±0.02	1.04	22.5	−18.8
	110	9.05±0.04			

a) Relative rates to that of **1** at 100 °C. b) 1 kcal mol^{-1} = 4.184 kJ mol^{-1}. c) 1 e. u. = 4.184 J K^{-1} mol^{-1}. d) Calculated from data at other temperatures. e) Calculated using absorbances at 50—65% completion of reaction and those at "infinity" estimated therefrom. Data of single runs were used.

Table 2. Trifluoroacetolysis products of ω-phenylalkyl menasylates

Substrate	Product	Yield (%)
3	$C_6H_5(CH_2)_3OCOCF_3$ (**7**)	35
	$C_6H_5CH_2CH(OCOCF_3)CH_3$ (**8**)	0[a]
	Indan (**9**)	0
4	$C_6H_5(CH_2)_4OCOCF_3$ (**10**)	0
	Tetralin (**11**)	100
5	$C_6H_5(CH_2)_5OCOCF_3$ (**12**)	12.3
	1-Methyltetralin (**13**)	65.2
	Benzocycloheptene (**14**)	12.0
6	$C_6H_5(CH_2)_6OCOCF_3$ (**15**)	14.8
	1-Ethyltetralin (**16**)	75.0

a) Decomposition was observed in the control experiment. At 75% completion of reaction, a 1 : 1 mixture of **7** and **8** was detected.

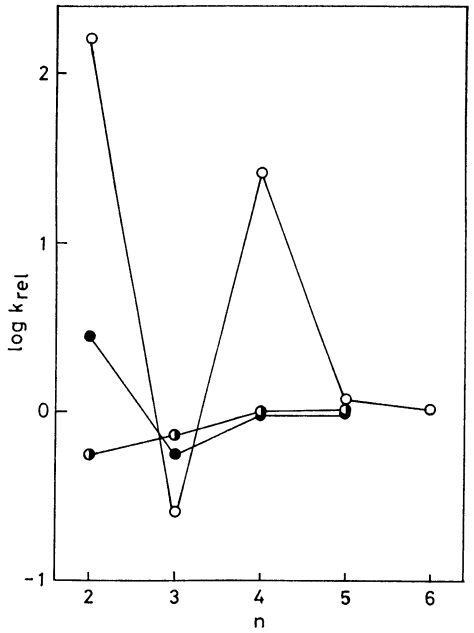


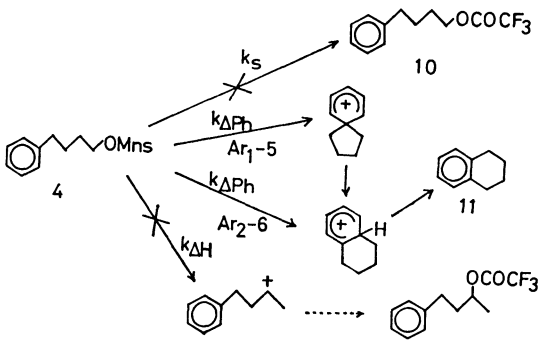
Fig. 1. Plots for logarithms of the relative rate constants of ω-phenylalkyl to butyl arenesulfonates *vs.* numbers of methylene groups.
○: Trifluoroacetolysis of menasylates at 100 °C, ●: formolysis of brosylates at 75 °C, ◑: acetolysis of brosylates at 75 °C.

assistance by a phenyl group, and the rate depression is attributable to the electron-withdrawing inductive effect of a phenyl group.

There have been many kinds of evidence that solvolysis of phenethyl esters is accelerated by anchimeric assistance of the neighboring phenyl group.[5] The fact that anchimeric assistance is usually pronounced in trifluoroacetic acid is also well-known.[2] On the other hand, evidence for anchimeric assistance by a phenyl group at delta to the reaction center has been very limited.[1,3,6-8] A rate enhancement with a factor of 26.2 indicates clearly the existance of such assistance. Another evidence was obtained from the study on the reaction products. In trifluoroacetolysis of **4**, the yield of tetralin (**11**) was quantitative and no other product was detected. As 4-phenylbutyl trifluoroacetate (**10**), a possible product of the solvent-assisted (k_s) pathway from **4**, was stable under the reaction conditions and did not give **11**, trifluoroacetolysis of **4** proceeds exclusively *via* the phenyl-assisted (k_Δ) pathway.

It is interesting to compare the rate enhancement factor of the δ-phenyl participation in the primary menasylates with that in the secondary tosylates. However, it is difficult to calculate the latter one because the reference tosylate was not solvolyzed under the same

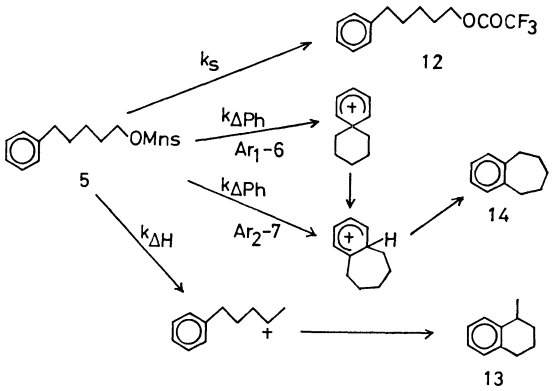
conditions. A rate ratio of 1-methyl-4-phenylbutyl tosylate to 1-methyl-5-phenylpentyl tosylate (6.6) is a good estimation for the enhancement. A corresponding ratio in the primary esters, **4** to **5**, is 22.1. A ratio of **4** to **6**, 25.2, may be a better estimation because the trifluoroacetolysis rate of **5** can not be considered as a standard (*vide infra*). The larger rate enhancement factor for the primary esters is quite reasonable as the electron demand in the form of anchimeric assistance is more pronounced in the primary solvolysis with a less stabilized reaction center than in the secondary solvolysis. The mechanism of trifluoroacetolysis of **4** is summarized in Scheme 1.



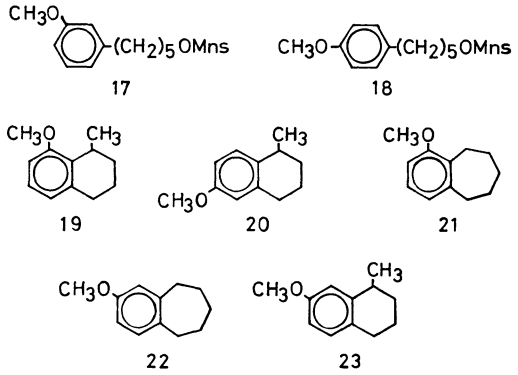
Scheme 1.

No new information was obtained from this study concerning the relative importance of the two possible modes of δ-phenyl participation, Ar_1-5 and Ar_2-6, proposed by Winstein.[1] It will be discussed in detail in a forthcoming paper.[9]

A small rate enhancement (18%) was also observed in trifluoroacetolysis of **5**. Inspection of the reaction products revealed that a 12.0% yield of 6,7,8,9-tetrahydro-5*H*-benzocycloheptene (**14**) was produced in the solvolysis. This is the first case of the production of a seven-membered ring compound through the k_Δ pathway by a carbon atom. By analogy to δ-phenyl participation, two modes of the reaction are possible in ε-phenyl participation; Ar_1-6 and Ar_2-7 (Scheme 2). In order to obtain information on the mechanism of this participation, 5-(*m*- and *p*-methoxyphenyl)pentyl menasylates (**17** and **18**) as well as **5** were solvolyzed under the same conditions. The rate constants and the reaction products were compared with each other (Table 3).



Scheme 2.



Since a methoxyl group is considered to activate its ortho and para positions and deactivate its meta positions, it was anticipated that introduction of a methoxyl group should have differentiated the two modes of participation. Unfortunately, however, introduction of a methoxyl group also caused the reactants and/or the products unstable under the reaction conditions. Because of faint discoloration of the reaction solutions at "infinity," the rate constants obtained involve much uncertainties. The yield of solvolysis products were also low especially in the case of the *m*-isomer (**17**). Nevertheless, a higher yield (16.8%) of 2-methoxy-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (**22**) from **18** than that of **14** (12.0%) from **5** indicates that activation of the ipso position by the *p*-methoxyl group contributes to an increase of the fraction of the k_Δ pathway. The result clearly verifies the importance of the Ar_1-6 pathway in ε-phenyl participation. Although no definite conclusion can be drawn concerning the Ar_2-7 pathway from a comparable yield (12.5%) of 1- and 2-methoxy-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (**21** and **22**) from **17**, we feel that the Ar_2-7 pathway also operates because deactivation of the ipso position by the *m*-methoxyl group does not decrease the fraction of the k_Δ pathway. A contribution from the Ar_2-7 pathway may compensate the ipso deactivation.

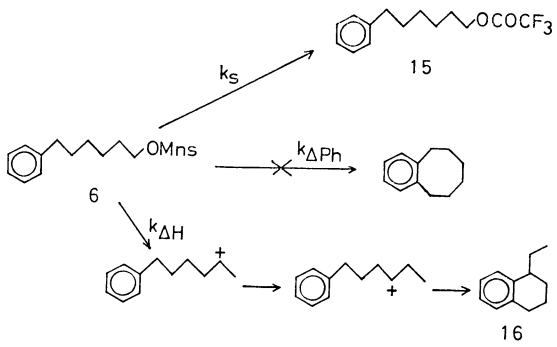
Table 3. Trifluoroacetolysis rates and products of 5-arylpentyl menasylates at 110 °C

Aryl	Rate $k_t \times 10^4/s^{-1}$	Product yield (%)		
		Prim. trifluoroacetate	1-Methyltetralin	Benzocycloheptene
C_6H_5 (**5**)	1.04±0.03	12.3	65.2	12.0
m-$CH_3OC_6H_4$ (**17**)	0.95[a]	12.6	28.2[b]	12.5[c]
p-$CH_3OC_6H_4$ (**18**)	0.99±0.06	14.0	50.4[d]	16.8[e]

a) The rate constant of a single run. b) The sum of yields of **19** (8.9%) and **20** (19.3%). c) The sum of yields of **21** (5.9%) and **22** (6.6%). d) A yield of **23**. e) A yield of **22**.

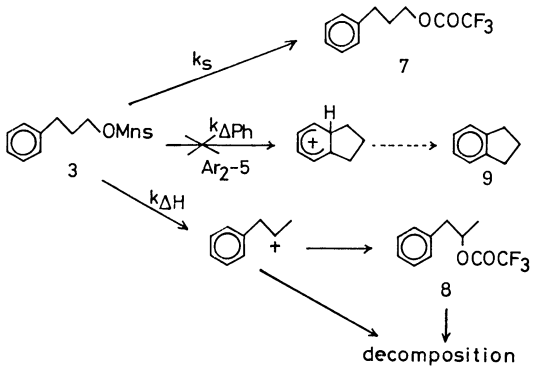
Formation of a large amount of 1-methyltetralin without a trace of a secondary trifluoroacetate from **5** is noteworthy. As it is well known that even a hydrogen next to the reaction center can participate in the solvolysis in trifluoroacetic acid, **5** must give 1-methyl-4-phenylbutyl cation or ion-pair at first.[10] The rate constant of this pathway should be designated as $k_{\Delta H}$ in contrast to that of the competitive pathway of phenyl participation as $k_{\Delta Ph}$. The cation must cyclize easily to give a 6-membered ring. A secondary trifluoroacetate (**6**) was found to be unstable in trifluoroacetic acid at a high temperature, although it was said stable at 29 °C.[3] Absence of secondary trifluoroacetates in the products from **3**, **5**, and **6** is attributed to their instability.

A phenyl ring at a more remote position than ε seems not to participate to the reaction center. The menasylate **6** was solvolyzed at a comparable rate with **1**. A small quantity (1.2%) of an unknown compound was detected by gas chromatography but its structure could not be identified as 5,6,7,8,9,10-hexahydrobenzocyclooctene. Hydrogen participation followed by hydrogen migration and cyclization is a possible route to 1-ethyltetralin (Scheme 3).



Scheme 3.

Inductive effects are considered to be transmitted to a more remote position in trifluoroacetic acid than in usual solvolysis solvents.[11] A distinct rate depression in **3** (k_{rel}=0.26) is clearly attributable to the electron-withdrawing inductive effect of a remote phenyl group. Indan, a possible product of the phenyl-assisted pathway, was not detected in the reaction mixture. In order to enhance the possibility of the Ar_2-5 pathway, the nucleophilicity of the ortho positions to the alkyl chain was increased by introduction of a methoxyl group at the meta position. Trifluoroacetolysis of 3-(*m*-methoxyphenyl)propyl menasylate (**24**), however, did not give methoxyindan at all. The rate constant for **24** was measured at 110 °C and similar to that of **3**. Accurate rate data could not be obtained because of discoloration of the reaction solutions. Reaction products from both of **3** and **24** were determined at the several stages of the reactions. About 1 : 1 mixtures of the primary and secondary trifluoroacetates were detected at the early stages of the reactions, but the latters decreased gradually and disappeared finally. Thus, the reaction of **3** is summarized in Scheme 4. The disadvantage of the Ar_2-5 pathway appears to be curious since indan is a stable and strain-free compound.



Scheme 4.

In the transition state of the phenyl-assisted pathway, however, the phenyl ring must approach to the reaction center from its perpendicular direction in order to ensure the p-σ overlap. The geometry is apparently a very unfavorable one for the Ar_2-5 pathway.[12]

Although the quantitative discussion on the activated parameters is difficult when the reaction includes composite pathways, useful information on the reaction is sometimes obtained from these parameters as they vary with the composition of the reaction. Relatively high entropies of activation have been considered a good criterion for anchimeric assistance besides rate enhancements and stereochemistry of reaction products.[13] In contrast to $\Delta S^{\neq}$ of *ca.* −17——18 e. u. (1 e. u.=4.184 J K^{-1} mol^{-1}) for the solvent-assisted (k_s) solvolysis, $\Delta S^{\neq}$ of *ca.* −7 e. u. for Ar_1-3 and *ca.* −10 e. u. for Ar_1-5 have been reported in ethanol, acetic acid, and formic acid.[1,13] Less negative $\Delta S^{\neq}$ for the anchimerically assisted (k_Δ) solvolysis can be attributed to a consequence of unimportance of nucleophilic involvement of the solvent in the transition state of the reaction. On the contrary, fairly constant and low $\Delta S^{\neq}$ were observed in trifluoroacetolysis throughout the series of ω-phenylalkyl menasylates; −15——16 e.u. for solvolysis with β and δ phenyl participation and −17——19 e.u. for others. As described above, most of the reactions in trifluoroacetic acid proceed *via* the k_Δ pathway in a sense; $k_{\Delta Ph}$ or $k_{\Delta H}$. Relatively constant $\Delta S^{\neq}$ can reasonably be expected in these cases. The low values of $\Delta S^{\neq}$ for the k_Δ pathway observed in this series are not anomalous in trifluoroacetic acid. $\Delta S^{\neq}$ for trifluoroacetolysis of ethyl tosylate, the pure k_s pathway, was −27 e.u. and much more negative than those in other solvents, *ca.* −17 e.u.[10] The differences of *ca.* 10 e.u. between $\Delta S^{\neq}$ in trifluoroacetic acid and those in other solvents observed in both of the k_Δ and k_s pathways suggest that electrophilic rather than nucleophilic solvation is important in trifluoroacetic acid and becomes a driving force of the reaction.

The effect of the concentration of sodium trifluoroacetate on the rates and the products was not studied in this series of solvolysis. It should be mentioned, however, that in trifluoroacetolysis of 4-phenylbutyl-1,1-d_2 menasylate (**4**-d_2) in the presence or absence of sodium trifluoroacetate, no deuterium scrambling was detected in the recovered menasylate. The cyclic intermediates of Ar_1-5 and/or Ar_2-6 pathways must afford tetralin without ion-pair return.

Experimental

General. All melting points were measured on a hot stage and not corrected. NMR spectra were recorded with Hitachi R-20 and R-24 spectrometers with tetramethylsilane as an internal standard.

Starting Alcohols. 1-Butanol and 3-phenyl-1-propanol were commercially available and used after purification. Other alcohols were prepared as follows.

4-Phenyl-1-butanol: This alcohol was prepared in a quantitative yield by lithium aluminum hydride reduction of 4-phenylbutanoic acid: bp 99—110 °C/4 Torr (lit,[14] 140 °C/14 Torr).

5-Phenyl-1-pentanol: This material was prepared by the Friedel-Crafts reaction of benzene with glutaric anhydride and aluminum chloride,[15] followed by the Wolff-Kishner reduction, esterification, and lithium aluminum hydride reduction, successively: bp 127 °C/5.5 Torr (lit,[14] 155 °C/20 Torr).

6-Phenyl-1-hexanol: This material was prepared by the Friedel-Crafts reaction of benzene with adipic anhydride polymer and aluminum chloride,[16] followed by the Wolff-Kishner reduction, esterification, and lithium aluminum hydride reduction, successively: bp 124 °C/3.5 Torr (lit,[14] 160—161 °C/13 Torr).

*3-(*m*-Methoxyphenyl)-1-propanol*: This alcohol was prepared by the Knoevenagel reaction of *m*-methoxybenzaldehyde with malonic acid,[17] followed by esterification and lithium aluminum hydride reduction: bp 137—138 °C/5.5 Torr (lit,[1] 135—140 °C/3.5 Torr).

*5-(*m*-Methoxyphenyl)-1-pentanol*: 3-(*m*-Methoxyphenyl)-1-propanol was converted to the chloride,[18] cyanide,[19] acid, ethyl ester, and 4-(*m*-methoxyphenyl)-1-butanol, successively. Application of the same series of reactions to the butanol gave the pentanol: bp 144—146 °C/3.5 Torr.

*5-(*p*-Methoxyphenyl)-1-pentanol*: This alcohol was prepared from 4-(*p*-methoxyphenyl)-1-butanol by the same sequence of reactions as described in the meta series: bp 147—148 °C/3 Torr (lit,[20] 144—145 °C/2 Torr).

4-Phenyl-1-butan-1,1-d_2*-ol*: This alcohol was prepared from ethyl 4-phenylbutanoate by reduction with lithium aluminum deuteride: bp 119.5 °C/6.5 Torr; deuterium content better than 99% (by ^{1}H NMR). Found: C, 78.91; H(D), 9.48% Calcd for $C_{10}H_{12}D_2O$: C, 78.90; H, 7.95; D, 1.32%.

Preparation of Menasylates. Menasylates were prepared by standard procedures from menasyl chloride and alcohols at 0°C in pyridine as a solvent.[4]

*Butyl Menasylate (**1**)*: Bp 177 °C/0.4 Torr, mp 33.7—34.7 °C. Found: C, 64.66; H, 6.48; S, 16.80%. Calcd for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52: S, 17.24%.

*Phenethyl Menasylate (**2**)*: Mp 104.3—105.0 °C (lit,[4] 101.9—102.5 °C).

*3-Phenylpropyl Menasylate (**3**)*: Mp 75.0—75.5 °C (from petroleum ether-ether). Found: C, 70.71; H, 5.75; S, 9.20%. Calcd for $C_{20}H_{20}O_3S$: C, 70.56; H, 5.92; S, 9.42%.

*4-Phenylbutyl Menasylate (**4**)*: Mp 104.9—105.0 °C (from hexane-benzene). Found: C, 71.36; H, 6.11; S, 9.17%. Calcd for $C_{21}H_{22}O_3S$: C, 71.16; H, 6.26; S, 9.06%.

*5-Phenylpentyl Menasylate (**5**)*: Mp 63.0—63.4°C (from cyclohexane). Found: C, 71.53; H, 6.27; S, 8.61%. Calcd for $C_{22}H_{24}O_3S$: C, 71.71; H, 6.57; S, 8.70%.

*6-Phenylhexyl Menasylate (**6**)*: Mp 52.0—52.8 °C (from petroleum ether-ether). Found: C, 72.08; H, 6.72; S, 8.33%. Calcd for $C_{23}H_{26}O_3S$: C, 72.22; H, 6.85; S, 8.38%.

*5-(*m*-Methoxyphenyl)pentyl Menasylate (**17**)*: This menasylate was obtained as an oil at a room-temperature and purified by recrystallization at a low temperature from petroleum ether-ehter. Found: C, 69.21; H, 6.45; S, 8.15%. Calcd for $C_{23}H_{26}O_4S$: C, 69.32; H, 6.58; S, 8.05%.

*5-(*p*-Methoxyphenyl)pentyl Menasylate (**18**)*: Mp 57.7—58.3 °C (from petroleum ether-ether). Found: C, 69.11; H, 6.55; S, 8.15%. Calcd for $C_{23}H_{26}O_4S$: C, 69.32; H, 6.58; S, 8.05%.

*3-(*m*-Methoxyphenyl)propyl Menasylate (**24**)*: Mp 46.0—47.0 °C (from petroleum ether-ether). Found: C, 67.81; H, 5.71; S, 8.70%. Calcd for $C_{21}H_{22}O_4S$: C, 68.08; H, 5.99; S, 8.65%.

4-Phenylbutyl-1,1-d_2 *Menasylate (**4**-*d_2*)*: Mp 104.5—105.0 °C (from ligroin); deuterium content better than 99% (by ^{1}H NMR). Found: C, 70.69; H(D), 6.13; S, 9.12%. Calcd for $C_{21}H_{20}D_2O_3S$: C, 70.76; H, 5.66; D, 0.56; S, 8.99%.

Preparation of Trifluoroacetates and Other Solvolysis Products. Authentic samples of trifluoroacetates were prepared from alcohols and three molar equivalents of trifluoroacetic anhydride at 0 °C. Excess of the anhydride was removed under reduced pressure and the residual esters were distilled. Indan (**9**) and tetralin (**11**) were purchased and purified.

*3-Phenylpropyl Trifluoroacetate (**7**)*: Bp 83—90 °C/5.5 Torr. Found: C, 56.98; H, 4.97; F, 24.21%. Calcd for $C_{11}H_{11}F_3O_2$: C, 56.90; H, 4.78; F, 24.55%.

*1-Methyl-2-phenylethyl Trifluoroacetate (**8**)*: Bp 67 °C/6 Torr (lit,[2a] 70—71 °C/5 Torr).

*4-Phenylbutyl Trifluoroacetate (**10**)*: Bp 91.1—92.0 °C/4 Torr. Found: C, 57.75; H, 5.32; F, 23.97%. Calcd for $C_{12}H_{13}F_3O_2$: C, 57.83; H, 5.26; F, 24.07%.

*5-Phenylpentyl Trifluoroacetate (**12**)*: Bp 77—78 °C/2 Torr. Found: C, 59.80; H, 5.95; F, 21.60%. Calcd for $C_{13}H_{15}F_3O_2$: C, 60.00; H, 5.81: F, 21.90%.

*6-Phenylhexyl Trifluoroacetate (**15**)*: Bp 96 °C/6 Torr. Found: C, 61.25; H, 6.44%. Calcd for $C_{14}H_{17}F_3O_2$: C, 61.31; H, 6.25%.

*6,7,8,9-Tetrahydro-5H-benzocycloheptene (**14**)*: This material was prepared by the Wolff-Kishner reduction of 6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one: bp 96.5-97.0 °C/13 Torr (lit,[21] 108—109 °C/22 Torr).

Trifluoroacetolysis Media. Trifluoroacetic acid containing 1 wt% of trifluoroacetic anhydride and 0.125 M of sodium trifluoroacetate was prepared according to the procedure described before.[4]

Kinetic Procedures. The usaul ampoule technique described before was employed.[4] Absorbances after more than ten half-lives were used as those at "infinity" except in the cases of **3**, **17**, and **18**. In these cases absorbances at infinity (A_∞) were calculated so as to make plots of $\log(A-A_\infty)$ *vs.* time linear. Absorbances were measured with a Hitachi Perkin-Elmer 139 UV-visible spectrophotometer.

Product Analyses. Reaction solutions containing 0.01 M of dodecane after more than seven half-lives were directly injected into a Varian Aerograph Model 2850-30 gas chromatograph with a flame ionization detector and a Hewlett-Packard 3370B digital integrator. A column packed with Silicon DC550 on Celite 545 was used. For the product analysis of **17**, PEG 20M on Celite 545 as a packing of a column and hexadecane as a standard were used. Sensitivities were determined using authentic samples for primary trifluoroacetates (**7**, **12**, and **15**), a secondary trifluoroacetate (**8**), tetralin (**11**), and 6,7,8,9-tetrahydro-5*H*-benzocycloheptene (**14**). For other compounds sensitivities were calculated by the method described by Sternberg *et al.*[22] Accuracy of calculated sensitivities were established for related compounds.

Identification of Solvolysis Products. All the reaction

products were separated by preparative gas chromatography and identified by comparison with authentic samples when available. Identification of following compounds were performed by spectroscopic analysis. NMR data in carbon tetrachloride are summarized below.

*1-Methyltetralin (**13**)*: δ=1.28 (3H, d, J=7.5 Hz, CH_3), 1.80 (4H, m), 2.80 (3H, m), and 7.07 (4H, m, Ar).

*1-Ethyltetralin (**16**)*: δ=0.95 (3H, t, J=7.5 Hz, CH_3), 1.80 (6H, m) 2.70 (3H, m), and 6.95 (4H, m, Ar).

*1-Methyl-8-methoxytetralin (**19**)*: δ=1.15 (3H, d, J=6.0 Hz, CH_3), 1.75 (4H, m), 2.73 (2H, m), 3.17 (1H, m), 3.77 (3H, s, OCH_3), and 6.42—7.00 (3H, m, Ar).

*1-Methyl-6-methoxytetralin (**20**)*: δ=1.18 (3H, d, J=8.0 Hz, CH_3), 1.67 (4H, m), 2.67 (3H, m), 3.59 (3H, s, OCH_3), and 6.40—7.05 (3H, m, Ar).

*1-Methoxy-6,7,8,9-tetrahydro-5H-benzocycloheptene (**21**)*: δ= 1.68 (6H, m), 2.72 (4H, m), 3.63 (3H, s, OCH_3), and 6.35 —6.92 (3H, m).

*2-Methoxy-6,7,8,9-tetrahydro-5H-benzocycloheptene (**22**)*: δ= 1.71 (6H, m), 2.70 (4H, m), 3.69 (3H, s, OCH_3), and 6.33— 6.92 (3H, m).

*1-Methyl-7-methoxytetralin (**23**)*: δ=1.22 (3H, d, J=7.5 Hz, CH_3), 1.75 (4H, m), 2.65 (3H, m), 3.60 (3H, s, OCH_3), and 6.30—6.85 (3H, m, Ar).

*Trifluoroacetolysis of 4-Phenylbutyl-1,1-d_2 Menasylate (**4**-d_2)*. A reaction solution of 0.05 M of **4**-d_2 in the same media as that for kinetic runs was allowed to react one half-life at 70.0 °C. The solvent was removed under reduced pressure and the residue was poured into ice-water. Precipitates were recovered by filtration and purified by recrystallization. No scrambling of the deuterium in the recovered **4**-d_2 was indicated by the absence of any signal at δ 4.06 (t, CH_2OMns).

A similar experiment in the absence of sodium trifluoroacetate also showed no scrambling of the deuterium in the recovered menasylate.

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